Divalent Lanthanoid Synthesis in Liquid Ammonia. 2. The Synthesis and X-ray Crystal Structure of $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$

Andrea L. Wayda,* Ishita Mukerji,[†] and James L. Dye[‡]

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Robin D. Rogers*

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received August 28, 1986

Dissolution of $Yb(C_8H_8)$ (synthesized via the reaction of ytterbium in liquid ammonia with C_8H_8) produces a green-brown solution (not deep red, as previously reported) from which deep red-black crystals of $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$ can be isolated and crystallographically characterized. The title compound crystallizes in the centric space group with unit-cell $P2_1/c$ dimensions $a = 10.055$ (4) Å, $b = 15.847$ (5) Å, $c = 28.354$ (9) Å, $\beta = 95.26$ (3)°, and $D_{calcd} = 1.63$ for $Z = 8$. Least-squares refinement resulted in a final R value of 0.062 ($R_w = 0.081$) based on 3350 independent observed [$F_o \geq 5\sigma(F_o)$] reflections. There are two molecules in the asymmetric unit. The overall structure is similar to a three-legged piano stool consisting of a symmetrically coordinated C_8H_8 dianion (COT^{2-}) and three N-bonded pyridine molecules. The average Yb–C and Yb–N distances are 2.64 (3) and 2.58 (2) Å, respectively. There is no evidence for short intermolecular contacts, and no nonbonded contacts are observed between the uncoordinated pyridine rings and the title compound. $Yb(t\text{-}C_4H_9C_8H_7)$ can be synthesized analogously and has chemical and physical properties similar to those of $Yb(C_8H_8)$.

Introduction

Divalent lanthanoid synthesis in liquid ammonia has proven to be a useful adjunct to standard metathetical schemes commonly employed in the synthesis of complexes in this important lanthanoid compound class. The utility of this method as an alternate synthetic route to known compounds was recently specifically demonstrated by the facile, high-yield synthesis of the divalent europium and ytterbium bis(pentamethylcyclopentadienides).[1] The method is generally applicable since it is easily extensible to other hydrocarbon substrates which are weak acids (other substituted cyclopentadienes, alcohols, phenols) or which are easily reduced (cyclooctatetraene and its derivatives).

As part of our continuing interest in divalent lanthanoid synthesis in liquid ammonia and as a complement to our studies of trivalent lanthanoid cyclooctatetraenides,[2a,b] we have reexamined the 1:1 reaction of ytterbium liquid ammonia solutions with cyclooctatetraene and *tert*-butylcyclooctatetraene. We report herein the results of this work and the crystal structure of the unusual tris(pyridine) adduct $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$.

Discussion and Results

Hayes and Thomas reported in 1969[3] that the 1:1 reaction of ytterbium and europium in liquid ammonia with cyclooctatetraene (COT) yielded $Yb(C_8H_8)$ and $Eu(C_8H_8)$, respectively. The compounds were described as highly air and moisture sensitive and insoluble in common organic solvents. However, in pyridine and DMF, solubility was achieved and deep red solutions were reported. We were intrigued by this communication since such an intense red color is normally not observed with pyridine solutions of divalent ytterbium complexes[4] and could be indicative of unusual associative effects and/or bonding in this highly coordinatively unsaturated compound.[5] Therefore, in order to establish the identity of the ytterbium species in pyridine solution, we re-examined the $Yb/NH_3/C_8H_8$ reaction system. At the same time, we investigated the effect of substitution on the solubility properties of 1:1 cyclooctatetraenides by studying the $Yb/NH_3/t\text{-}C_4H_9C_8H_7$ reaction system.

Ytterbium in liquid ammonia quickly reacts with cyclooctatetraene to yield a fine solid which exhibits different colors depending upon the solvent contacting its surface. When initially formed, the observed suspended solids are yellow-green. As the reaction goes to completion, the precipitated product assumes a uniform orange color. Washing this product with freshly distilled ammonia followed by removal of the final traces of ammonia by pumping at high vacuum results in the formation of a free-flowing bright pink-purple powder.

The material is formulated as $Yb(C_8H_8)$ on the basis of complexometric metal analysis and infrared spectroscopy and by comparison of its properties with those reported by Hayes and Thomas.[3] The compound is totally insoluble in pentane, ether, toluene, Me_3N, and THF. Solid in contact with these solvents retains the color of the free-flowing powder. When contacted with fresh liquid ammonia or $MeNH_2$, no solubility is observed but the solid assumes an orange and yellow-orange color, respectively. Removal of these solvents regenerates the pink-purple color. These observations confirm the original report of Hayes and Thomas. In contrast, however, we find that dissolution of $Yb(C_8H_8)$ in rigorously purified pyridine[6]

[†] Work performed while at AT&T-BL. Present address: Graduate Chemistry Department, University of California, Berkeley, CA.

[‡] Work performed while on sabbatical leave from Michigan State University, East Lansing, MI 48824.

(1) Wayda, A. L.; Dye, J. L; Rogers, R. D. *Organometallics* 1984, *3*, 1605.

(2) (a) Wayda, A. L. *Organometallics* 1983, *2*, 565. (b) Wayda, A. L.; Rogers, R. D. *Organometallics* 1985, *4*, 1440.

(3) Hayes, R. G.; Thomas, J. L. *J. Am. Chem. Soc.* 1969, *91*, 6876.

(4) However, medium purple colors are sometimes observed (see ref 1 and 7).

(5) By conventional assignment, $Yb(C_8H_8)$ has a formal coordination number of 5. Divalent ytterbium complexes normally exhibit coordination numbers of 6–8.

0276-7333/87/2306-1328$01.50/0

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$(\eta^8\text{-}C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$
mol wt	553.54
space group	$P2_1/c$
cell constants	
a, Å	10.055 (4)
b, Å	15.847 (5)
c, Å	28.354 (9)
β, deg	95.26 (3)
cell vol, Å^3	4498.9
molecules/unit cell	8
ρ(calcd), g cm^{-3}	1.63
μ(calcd), cm^{-1}	43.78
radiation	Mo Kα
max cryst dimens, mm	0.40 × 0.60 × 1.00
scan width	$0.75 + 0.20 \tan \theta$
std reflctns	$(0,\overline{12},0)$, $(\bar{7},0,0)$, $(0,0,\overline{24})$
decay of stds	±1%
reflctns measd	5119
2θ range	$2 \leq 2\theta \leq 50°$
reflctns obsd $[F_o \geq 5\sigma(F_o)]$	3350
no. of parameters varied	361
weighting scheme	$[(1/\sigma_{F_o}^2 - 1/0.0007F_o)]$
GOF	2.1
R	0.062
R_w	0.081

does not yield a deep red solution as reported but a green-brown solution which, as stated previously, we have observed to be one of the characteristic colors of divalent ytterbium complexes. The compound is only slightly soluble in pyridine and can be crystallized by slow vapor-phase diffusion of pentane into a saturated pyridine solution of the compound at ambient pressure and temperature. Crystals obtained in this manner are deep red-black in color. When removed from the mother liquor, they immediately desolvate (within minutes) crumbling into a finely dispersed pink-purple solid. This instability of the crystals to efflorescence precluded normal spectroscopic characterization or chemical analysis. Hence, an X-ray structure determination was necessary not only to reveal the detailed coordination environment of the metal but also to establish the identity of the compound. This study reveals the complex to be a tris(pyridine) adduct of $Yb(C_8H_8)$ exhibiting *no* close nonbonded contacts. We therefore conclude that the true color of the pyridine solution of $Yb(C_8H_8)$ is well within the range normally observed for divalent ytterbium species and that the crystal structure of the pyridine adduct isolated from this solution indicates no unusual bonding or associative features.

By comparison, the reaction chemistry of Yb/NH_3 solution with a substituted cyclooctatetraene, $t\text{-}C_4H_9\text{–}C_8H_7$, closely parallels that of the $Yb/NH_3/C_8H_8$ reaction system. The 1:1 reaction of ytterbium in liquid ammonia with $t\text{-}C_4H_9\text{–}C_8H_7$ proceeds smoothly to yield a yellow-gold ammonia-insoluble powder. Removal of ammonia generates a bright pink-purple compound identical in hue with that of $Yb(C_8H_8)$. Unfortunately, the increased steric bulk of the substituted cyclooctatetraene does not confer enhanced solubility on the product. As is $Yb(C_8H_8)$, $Yb(t\text{-}C_4H_9\text{–}C_8H_7)$ is insoluble in all common organic solvents but is slightly soluble in rigorously purified pyridine. Crystallization attempts identical with those successful for $Yb(C_8H_8)$ only result in precipitation of the compound. In lieu of structural analysis, the compound can be satisfactorily characterized by complexometric metal analysis and infrared spectroscopy.

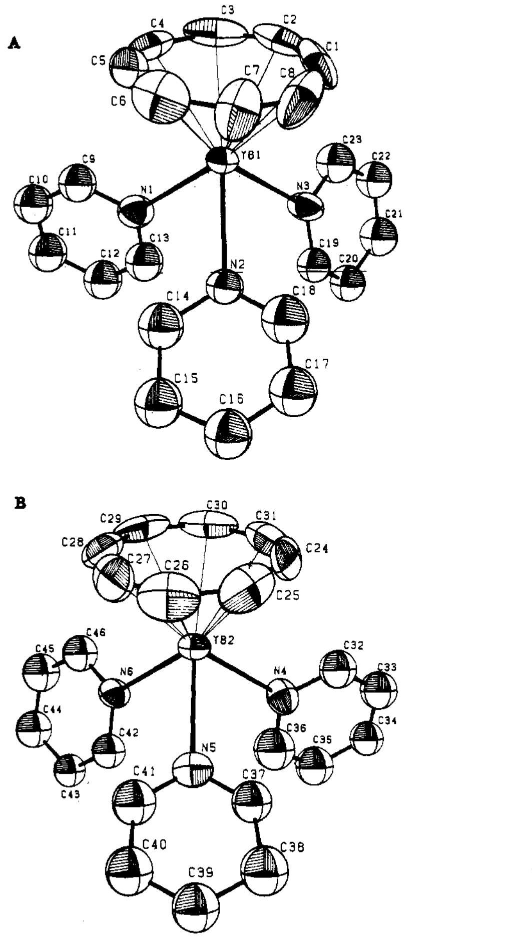

Figure 1. Molecular structures and atom labeling schemes for the two (A and B) independent $(\eta^8\text{-}C_8H_8)Yb(C_5H_5N)_3$ molecules in the asymmetric unit. The atoms are represented by their 50% probability ellipsoids, and the hydrogen atoms have been omitted.

Table II. Selected Bond Distances (Å) and Angles (deg)

molecule A		molecule B	
	Bond Distances		
Yb(1)–N(1)	2.59 (1)	Yb(2)–N(4)	2.57 (1)
Yb(1)–N(2)	2.56 (1)	Yb(2)–N(5)	2.56 (1)
Yb(1)–N(3)	2.57 (1)	Yb(2)–N(6)	2.61 (1)
N–C(av)	1.34 (4)	N–C(av)	1.33 (4)
C–C(av)	1.37 (4)	C–C(av)	1.38 (2)
Yb(1)–C(1)	2.63 (2)	Yb(2)–C(24)	2.66 (2)
Yb(1)–C(2)	2.69 (2)	Yb(2)–C(25)	2.61 (2)
Yb(1)–C(3)	2.67 (2)	Yb(2)–C(26)	2.68 (2)
Yb(1)–C(4)	2.62 (2)	Yb(2)–C(27)	2.63 (2)
Yb(1)–C(5)	2.63 (2)	Yb(2)–C(28)	2.64 (2)
Yb(1)–C(6)	2.61 (2)	Yb(2)–C(29)	2.68 (2)
Yb(1)–C(7)	2.60 (2)	Yb(2)–C(30)	2.66 (2)
Yb(1)–C(8)	2.57 (2)	Yb(2)–C(31)	2.61 (2)
C–C(av)	1.4 (1)	C–C(av)	1.39 (9)
Cent1–Yb(1)	1.91	Cent2–Yb(2)	1.92
	Bond Angles		
N(1)–Yb(1)–N(2)	83.2 (4)	N(4)–Yb(2)–N(5)	82.1 (5)
N(1)–Yb(1)–N(3)	88.2 (5)	N(4)–Yb(2)–N(6)	89.5 (4)
N(2)–Yb(1)–N(3)	84.4 (4)	N(5)–Yb(2)–N(6)	84.9 (4)
Cent1–Yb(1)–N(1)	130.1	Cent2–Yb(2)–N(4)	128.5
Cent1–Yb(1)–N(2)	128.5	Cent2–Yb(2)–N(5)	128.6
Cent1–Yb(1)–N(3)	126.9	Cent2–Yb(2)–N(6)	127.9
C–C–C(av)	135 (1)	C–C–C(av)	135 (4)

Molecular Structure of $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$. As is often the case, the lack of good quality crystals has severely affected the quality of the structural results. However, the structural features of this compound are of sufficient interest and the results of sufficient quality

---

(6) Pyridine purified by the normal protocol for this solvent (drying over KOH, followed by distillation from BaO under argon) is insufficiently dry for our purposes.

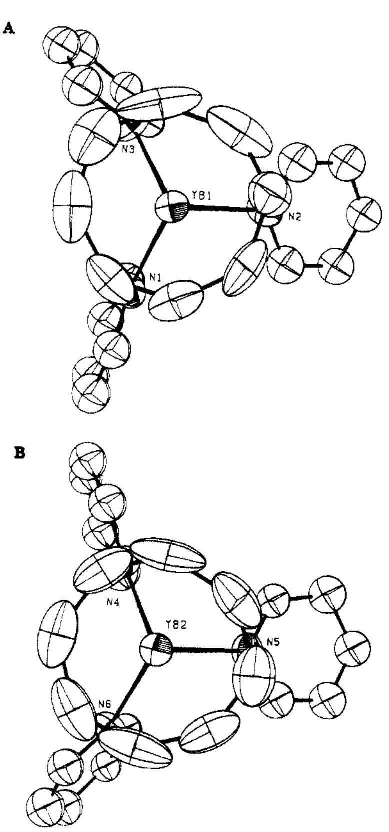

Figure 2. Top view A and B showing the differences in pyridine ring twists relative to the η^8-C_8H_8 plane.

to make general comparisons with similar structures useful. The molecular structures and atom labeling schemes for the two independent molecules are presented in Figure 1. Some important bond distances and angles are given in Table II.

The two molecules in the asymmetric unit are mirror images. This is readily seen from the coordinates in Table I and the ORTEP's in Figure 1. It was not possible to find a space group that would suitably relate the two molecules (see Experimental Section). Each ytterbium atom is eight-coordinate; the five electron pairs of the cyclooctatetraenide ligand occupy five formal coordination sites with the remaining three involved in ytterbium–pyridine interactions. The overall geometry at each metal center is not unlike that observed for (η^8-C_8H_8)Ln[*o*-$C_6H_4CH_2N(CH_3)_2$](OC_4H_8).[2b]

The tripod base of the molecule consists of three pyridine ligands directed linearly away from each ytterbium atom. (The average Yb–N–centroid (pyridine) angle is 173 (4)°). The pyridine ligands are coordinated to the metals through the nitrogen atoms at an average Yb–N separation of 2.58 (2) Å. This is essentially the same value observed in the other structurally characterized eight-coordinate Yb(II) pyridine complex (η^5-$C_5Me_5)_2Yb(C_5H_5N)_2$[7] (2.56 (3) Å. It is also near the 2.55 (3) Å Yb–NH_3 distance found for (η^5-$C_5Me_5)_2Yb(NH_3)(C_4H_8O)$.[1] In the title compound, the planes defined by the pyridine rings are canted with respect to each other (Figure 2) and intersect with dihedral angles which average 66 (6)°. For comparison, the planes defined by the pyridine rings in (η^5-$C_5Me_5)_2Yb(C_5H_5N)_2$ intersect at an angle of 56°. Another parameter which quantitates the relative canting of the pyridine ring planes is the angle between the pyridine plane and that of the cyclooctatetraenide ring. This angle ranges from 26° for the N(2) and N(5) planes (Yb(1) and Yb(2), respectively) to 98° for the N(1) and N(4) planes. In the title compound, the average centroid (COT)–Yb–N and N–Yb–N angles are 128 (1)° and 85 (3)°, respectively.

The cyclooctatetraenide ligands behave as planar aromatic dianions. The C–C distances average 1.39 (5) Å and the C–C–C angles 135 (2)° (identical with the ideal values of 1.40 Å and 135°). Both rings are planar to within 0.04 Å.

As noted in the Introduction, we are interested in the structural characterization of a series of cyclooctatetraene/lanthanoid derivatives in order to more fully characterize the metal–ring interaction and the behavior of the cyclooctatetraene dianion (COT^{2-}) ligand itself. Presently, there are few such structures which can be used to compare with the title compound. The Yb–C distances average 2.64 (3) Å and range from 2.57 (2) to 2.69 (2) Å. These distances are shorter, as expected, than the Yb–C separations for the ten-coordinate Yb(II) ion in $[K(C_4H_{10}O_2)]_2[Yb(C_8H_8)_2]$[12] (2.74 (3) Å). If we assume a value of 1.14 Å for the effective ionic radius of eight-coordinate Yb(II),[8] the effective ionic radius of the COT dianion is calculated to be 1.50 Å. In the predominantly ionic lanthanoid series compounds, this latter value is useful in comparing metal–COT^{2-} interactions between different metals in different oxidation states and geometries. The 1.50-Å effective ionic radius for the COT dianion in the title compound is in good agreement with the 1.49-Å value calculated for $[K((CH_3OCH_2CH_2)_2O)][Ce(C_8H_8)_2]$[9] and the 1.50-Å value in $[Ce(C_8H_8)Cl\cdot 2(C_4H_8O)]_2$.[10] The effective ionic radius for ten-coordinate Nd(III) was not avaliable for a comparison with $[Nd(C_8H_8)(C_4H_8O)_2][Nd(C_8H_8)_2]$.[11] Using our calculated effective ionic radius of the COT dianion of 1.50 Å, we calculate an effective ionic radius for ten-coordinate Yb(II) of 1.24 Å in $[K(C_4H_{10}O_2)]_2[Yb(C_8H_8)_2]$.[12]

Finally, we note that there are no unusually short intermolecular contacts and there are no nonbonded contacts between the uncoordinated pyridine rings and the title compound (<4.0 Å).

Conclusions

Our reinvestigation of the synthesis of $Yb(C_8H_8)$ via the reaction of ytterbium in liquid ammonia with cyclooctatetraene show the original work and observations of Hayes and Thomas to be substantially correct. However, their intriguing report of the deep red color of $Yb(C_8H_8)$ in pyridine has not been reproducible in our hands. We find instead a green-brown solution (characteristic of divalent ytterbium complexes) from which crystals of the tris(pyridine) adduct $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$ can be isolated and crystallographically characterized. This determination reveals that the extremely coordinatively unsaturated complex $Yb(C_8H_8)$ completes its coordination sphere in pyridine by the formation of three adduct bonds. Although intermolecular interactions between ytterbium and the delocalized electron density of the C_8H_8 dianion must be important in the solid-state structure of this material, these interactions are not strong enough to

---

[7] Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647.

[8] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

[9] Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 3030.

[10] Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 171.

[11] DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625.

[12] Kinsley, Streitwieser, and Zalkin have recently demonstrated (*Organometallics* **1985**, *4*, 52) the profound effect of ligand number and coordinative saturation on the solubility of cyclooctatetraenide derivatives with their synthesis of the 1:2 COT derivative $K_2Yb(C_8H_8)_2$.

survive dissolution in pyridine. Substitution of the cyclooctatetraene ring does not substantially affect the chemical and physical properties of 1:1 ytterbium cyclooctatetraenide complexes.[12]

Experimental Section

General Data. The extremely air- and moisture-sensitive compounds are handled in the recirculated argon atmosphere of a Vacuum Atmospheres HE-43 drybox. All glassware in contact with metal ammonia solutions has been washed with HF cleaner (60% H_2O, 30% HNO_3, 5% HF, Alconox) to eliminate surface contaminants capable of catalyzing decomposition. A full description of the vaccum line system and ancillary equipment used in this work has been published elsewhere.[13]

Materials. Ytterbium metal powder was obtained from Research Chemicals, Phoenix, AZ. Electronic grade ammonia was obtained from Matheson and was predried over a freshly distilled mirror of high purity sodium or potassium (Alfa) immediately before use. THF, toluene, and ether were distilled from sodium benzophenone ketyl under argon. Pentane was distilled from sodium benzophenone ketyl (stabilized by the addition of tetraglyme) under argon. Me_3N and $MeNH_2$ were dried and degassed by transferring the amine onto a mixture of solid sodium and benzophenone. After the deep blue color of the ketyl had developed, the amines were then vacuum transferred into a stainless-steel Hoke-valved storage cylinder and used as needed. Pyridine was distilled from sodium under argon. Cyclooctatetraene (Aldrich) and *tert*-butylcyclooctatetraene (MSU Synthesis Labs) were dried over activated 4-Å molecular sieves and degassed by vacuum transfer.

Measurements. Infrared spectra were recorded on solid samples that had been mulled with dry degassed Nujol and sandwiched between 25 × 4 mm NaCl plates protected from the atmosphere in an O-ring-sealed Barnes Presslok holder. Spectra were recorded with a Nicolet 5 DX FT-IR spectrometer. Complexometric metal analyses were conducted as described previously.[14]

$(C_8H_8)Yb$ and $(C_8H_8)Yb(C_5H_5N)_3\cdot{}^1/_2C_5H_5N$. Reaction of 0.313 g (1.81 mmol) of ytterbium powder with 0.187 g (1.80 mmol) of C_8H_8 in liquid ammonia (C_8H_8 transferred onto the blue metal–ammonia solution at −196 °C) yielded a yellow-green finely divided powder (reaction time ~24 h at −20 to −35 °C). The crude product was then washed several times with ammonia. During washing, the initial yellow-green product changed color to a medium orange. Complete removal of ammonia on the vacuum line resulted in a final dramatic color change to a bright pink-purple. Removal of the reaction cell to the drybox allowed the isolation of 0.390 g (78% yield) of $(C_8H_8)Yb$.

As previously reported, the compound is totally insoluble in all common organic solvents (see text for details): IR (Nujol mull, cm^{-1}) 890 (s), 670 (s). Anal. Calcd for $(C_8H_8)Yb$: Yb 62,4. Found: Yb, 64.5. Red-black crystals of the complex suitable for X-ray diffraction can be grown by slow diffusion of pentane onto a saturated green-brown pyridine solution of the compound at ambient temperature and atmospheric pressure. Infrared and complexometric metal analysis characterization studies are precluded by the extremely rapid efflorescence of the compound in the desolvating atmosphere of the drybox.

$(t\text{-}C_4H_9\text{–}C_8H_7)Yb$. Reaction of 0.8655 g (5.0 mmol) of ytterbium powder with 0.8005 g (5.0 mmol) of $t\text{-}C_4H_9\text{–}C_8H_7$ yielded a finely divided green powder (ytterbium–ammonia solution poured onto the substituted cyclooctatetraene; complete transfer of the metal effected by back-distillation of ammonia and transfer of residual metal via redissolution; reaction time ~24 h at −20 to −35 °C). Washing the crude product with ammonia produced a yellow-gold powder. After complete removal of ammonia at medium and high vacuum, the compound assumed a bright pink-purple hue identical with that of $(C_8H_8)Yb$. The reaction cell was then removed to the drybox for product isolation and characterization (1.3127 g, 79% yield: IR (Nujol mull, cm^{-1}) 1222 (m), 934 (m), 857 (m), 744 (m), 702 (s). Anal. Calcd for $Yb(C_4H_9\text{–}C_8H_7)$: Yb, 51.92. Found: Yb, 49.95.

Table III. Final Fractional Coordinates for $(\eta^8\text{-}C_8H_8)Yb(NC_5H_5)_3\bullet{}^1/_2NC_5H_5$[a]

atom	*x/a*	*y/b*	*z/c*
Yb(1)	0.09125 (6)	0.12252 (4)	0.87625 (2)
Yb(2)	0.65522 (6)	0.12408 (4)	0.62883 (2)
N(1)	0.143 (1)	0.2019 (9)	0.9556 (5)
N(2)	−0.016 (1)	0.2633 (8)	0.8493 (5)
N(3)	0.305 (1)	0.1872 (8)	0.8484 (6)
N(4)	0.660 (1)	0.1972 (9)	0.5482 (5)
N(5)	0.567 (1)	0.2682 (8)	0.6522 (5)
N(6)	0.890 (1)	0.1870 (8)	0.6551 (5)
C(1)	0.128 (3)	0.001 (2)	0.816 (1)
C(2)	0.193 (2)	−0.028 (1)	0.855 (1)
C(3)	0.165 (2)	−0.035 (1)	0.900 (1)
C(4)	0.048 (2)	−0.013 (1)	0.9256 (7)
C(5)	−0.067 (2)	0.015 (1)	0.9145 (9)
C(6)	−0.139 (2)	0.046 (1)	0.874 (1)
C(7)	−0.113 (2)	0.056 (2)	0.8262 (8)
C(8)	−0.012 (3)	0.042 (2)	0.8031 (8)
C(9)	0.093 (2)	0.168 (1)	0.9946 (7)
C(10)	0.112 (2)	0.203 (1)	1.0391 (8)
C(11)	0.178 (2)	0.276 (1)	1.0432 (8)
C(12)	0.231 (2)	0.312 (1)	1.0043 (8)
C(13)	0.205 (2)	0.275 (1)	0.9614 (8)
C(14)	−0.096 (2)	0.307 (1)	0.8778 (8)
C(15)	−0.172 (2)	0.379 (1)	0.8606 (7)
C(16)	−0.167 (2)	0.399 (1)	0.8141 (7)
C(17)	−0.092 (2)	0.356 (1)	0.7862 (8)
C(18)	−0.019 (2)	0.291 (1)	0.8057 (8)
C(19)	0.328 (2)	0.266 (1)	0.8435 (6)
C(20)	0.446 (2)	0.300 (1)	0.8333 (7)
C(21)	0.552 (2)	0.240 (1)	0.8245 (8)
C(22)	0.521 (2)	0.157 (1)	0.8265 (7)
C(23)	0.406 (2)	0.131 (1)	0.8421 (7)
C(24)	0.467 (3)	0.020 (2)	0.591 (1)
C(25)	0.421 (2)	0.057 (1)	0.637 (1)
C(26)	0.476 (3)	0.064 (1)	0.685 (1)
C(27)	0.595 (3)	0.039 (1)	0.7035 (8)
C(28)	0.714 (3)	0.001 (1)	0.690 (1)
C(29)	0.757 (2)	−0.029 (1)	0.650 (1)
C(30)	0.702 (3)	−0.033 (1)	0.602 (1)
C(31)	0.575 (3)	−0.008 (1)	0.5795 (8)
C(32)	0.598 (2)	0.163 (1)	0.5087 (7)
C(33)	0.604 (2)	0.197 (1)	0.4641 (7)
C(34)	0.671 (2)	0.269 (1)	0.4577 (7)
C(35)	0.737 (2)	0.306 (1)	0.4969 (8)
C(36)	0.725 (2)	0.273 (1)	0.5410 (8)
C(37)	0.472 (2)	0.304 (1)	0.6258 (7)
C(38)	0.386 (2)	0.370 (1)	0.6381 (7)
C(39)	0.419 (2)	0.400 (1)	0.6844 (7)
C(40)	0.519 (2)	0.365 (1)	0.7125 (7)
C(41)	0.588 (2)	0.299 (1)	0.6949 (8)
C(42)	0.921 (2)	0.268 (1)	0.6569 (6)
C(43)	1.042 (2)	0.300 (1)	0.6732 (6)
C(44)	1.145 (2)	0.243 (1)	0.6895 (8)
C(45)	1.106 (2)	0.160 (1)	0.6864 (7)
C(46)	0.985 (2)	0.132 (1)	0.6688 (6)
X(1)[P(1)]	0.100 (3)	0.537 (2)	1.020 (1)
X(2)[P(1)]	0.056 (3)	0.556 (2)	0.972 (1)
X(3)[P(1)]	−0.045 (3)	0.513 (2)	0.952 (1)
X(1)[P(2)]	0.555 (2)	0.558 (2)	0.527 (1)
X(2)[P(2)]	0.475 (2)	0.515 (2)	0.5458 (9)
X(3)[P(2)]	0.416 (3)	0.457 (2)	0.519 (1)

[a] X positions correspond to the disordered pyridine rings. Each was refined as 17% N and 83% C.

X-ray Data Collection, Structure Determination, and Refinement. The title compound was very difficult to crystallize. This necessitated the use of a rather large 0.40 × 0.60 × 1.00 mm crystal which was sealed under nitrogen in a thin-walled glass capillary. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 14°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection pa-

---

[13] Wayda, A. L.; Dye, J. L. *J. Chem. Educ.* **1985**, *62*, 356.

[14] Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

rameters is given in Table I. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction using ψ scans of $\chi - 90°$ reflections was employed.

Calculations were carried out with the SHELX system of computer programs.[15] Neutral atom scattering factors for Yb, N, C, and H were taken from ref 16, and the scattering was corrected for the real and imaginary components of anomalous dispersion.

The positions of the ytterbium atoms were revealed by using the direct methods program MULTAN. Difference Fourier maps phased on the ytterbium atoms revealed the positions of the non-hydrogen atoms. Two pyridine rings not associated with the ytterbium atoms were also located around centers of inversion. These rings were treated as completely disordered at each position (X in Table III) and refined as $^1/_6$ N and $^5/_6$ C.

Early in the data analysis, it appeared that the two independent molecules in the asymmetric unit were possibly symmetry related. An investigation of the positional parameters, space group, and final ORTEPs indicated that although the two molecules were mirror images of each other, the choice of space group ($P2_1/c$) was correct.

The size of the crystal used in this study and the large number of independent variables posed several problems in the refinement of the structure. Hence, the ytterbium atoms, coordinated nitrogen atoms, and the cyclooctatetraene carbon atoms were refined anisotropically, while the remaining carbon atoms were refined isotropically. The disordered pyridine rings were also refined isotropically. The hydrogen atom contributions were included in calculated positions (0.95 Å from the bonded carbon) for all but the uncoordinated pyridine rings and allowed to ride with B fixed on the appropriate carbon atom. This refinement led to final values of $R = 0.062$ and $R_w = 0.081$. A final difference Fourier showed no feature greater than 1.2 e/Å^3. The weighting scheme was based on $[(1/\sigma_{F_o}{}^2) + (1/pF_o{}^2)]$ when $p = 0.0007$; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table III.

Acknowledgment. R.D.R. wishes to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF Chemical Instrumentation Program for partial support of this work. A.L.W. thanks Prof. T. Don Tilley for helpful discussions of pyridine purification procedures.

Supplementary Material Available: Tables of thermal parameters, bond distances and angles, least-squares planes, and H-atom fractional coordinates (8 pages); listings of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

---

(15) Sheldrick, G. M., SHELX, a system of computer programs for X-ray structure determination as locally modified.

(16) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149.

(17) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* 1971, *A27*, 368.

(18) See paragraph at end of paper regarding supplementary material.

Structural and Molecular Orbital Probes into the H/AuPR$_3$ Isolobal and Isostructural Analogy: Fe$_4$(CO)$_{12}$(AuPPh$_3$)$_2$BH vs. Fe$_4$(CO)$_{12}$BH$_3$

Catherine E. Housecroft*†

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

Arnold L. Rheingold*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received October 20, 1986

The preparation and crystal structure of the compound $Fe_4(CO)_{12}(AuPPh_3)_2BH$ are reported: triclinic, $P\bar{1}$, $a = 10.870$ (3) Å, $b = 12.114$ (3) Å, $c = 20.466$ (6) Å, $\alpha = 80.23$ (2)°, $\beta = 83.17$ (2)° $\gamma = 73.40$ (2)°, $V = 2537.9$ Å^3, $Z = 2$; $R_F = 4.49\%$. The new cluster is related to the known ferraborane $Fe_4(CO)_{12}BH_3$ by the replacement of two endo-hydrogen atoms by gold(I) triphenylphosphine units. However, the ferraborane and its aura derivative are not structurally analogous; the H/AuPR$_3$ substitution causes the "migration" of a hydrogen (in the form of AuPPh$_3$) from the metal framework toward the boron atom, thus causing the latter to be associated with six metal atoms. A boridic environment is therefore exemplified in the new cluster. Analysis of the molecular structure of $Fe_4(CO)_{12}(AuPPh_3)_2BH$ suggests that each AuPPh$_3$ unit is primarily associated with an iron-boron edge. Fenske-Hall calculations, which use CuPH$_3$ to model AuPPh$_3$, confirm the latter bonding description of the cluster. For $Fe_4(CO)_{12}BHX_2$ (X = H or CuPH$_3$), the preferences for a given isomer structure are examined within the framework of the Fenske-Hall calculations. The role played by the iron tricarbonyl units in "freezing" either a proton or an AuPR$_3^+$ unit into a particular site on the cluster surface is found to be significant. The isolobal analogy between H$^+$, CuPH$_3^+$, and AuPR$_3^+$ is supported by the results of the calculations even though $Fe_4(CO)_{12}BH_3$ and $Fe_4(CO)_{12}(AuPPh_3)_2BH$ are not structurally analogous.

The ability of the Lewis acid AuPR$_3^+$ to mimic H$^+$ through replacement in a transition-metal cluster is now well-established.[1-4] A few examples of H/AuPR$_3$ replacement in borane clusters are documented,[5] but the majority of examples of this isolobal relationship are found in transition-metal hydride cluster chemistry. Compounds in which one or more endo-hydrogen atoms have been replaced by gold fragments have been observed. When a single hydrogen atom is replaced, a structural analogy

---

† Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

(1) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* 1981, *103*, 7648.

(2) Bateman, L. W.; Green, M.; Mead, K. A.; Mills, R. M.; Salter, I. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* 1983, 2599.

(3) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* 1984, *32*, 237 and references therein.

(4) Horowitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* 1985, *107*, 8136 and references therein.

0276-7333/87/2306-1332$01.50/0